Zinc Complexes Increase Uptake of Zn by Plants: Dependence of Critical Zn^{2+} Activity on Ligand Type

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INTRODUCTION

Nutrient solutions are well-defined media, and have proved useful to study plant mineral nutrition. Since it is difficult to impose Zn deficiency in conventional nutrient solutions (Parker et al. 1995), chelator-buffered solutions, which allow maintaining Zn^{2+} activity at low and well-controlled levels, have frequently been used to study Zn deficiency. Most of these studies have suggested critical Zn^{2+} activities around $10^{-10.5}$ M (or pZn 10.5), below which plant yield is reduced (e.g. Chaney et al. 1989).

We found previously that Cd complexes contribute to Cd uptake by spinach (Degryse et al. 2006a). If complexes also contribute to Zn uptake, the critical Zn^{2+} activity in chelator-buffered solution is expected to depend on the type of ligand, and to be smaller than in a solution without Zn complexes. This hypothesis was tested by measuring Zn uptake in chelator-buffered and resin-buffered solutions.

METHODS

Zinc deficiency was assessed in chelator (CDTA or HEDTA)-buffered nutrient solutions (with total Zn 10^{5} or $10^{4.5}$ times higher than the free Zn^{2+} concentration) or in solutions without a soluble ligand where Zn was buffered with a solid phase resin (Chelex). The plants (spinach or tomato) were grown for 17 days on continuously aerated solutions, and pH was maintained at 6.0±0.1. At harvest, plants were weighed, dried and the metal concentrations in shoot and root were analysed with Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) after hot acid digestion.

In another experiment, Zn uptake by spinach was measured in chelator-buffered solutions with free Zn^{2+} concentration of 10^{-9} M and total Zn concentration of 10^{-5} M, using complexes with varying dissociation rates (as measured with a competitive ligand exchange method). The plants were taken from the nutrient solutions at 19 days after transplanting. Details of the methods can be found elsewhere (Degryse et al. 2006b).

RESULTS AND DISCUSSION

Zinc deficiency symptoms (stunting, chlorosis) were observed in HEDTA-buffered solutions at pZn ≥ 10.5. In CDTA-buffered solutions, Zn deficiency was observed at higher Zn^{2+} activities (pZn ≥ 10.2). In resin-buffered solutions, weak symptoms (comparable to those in HEDTA-buffered solutions at pZn 10.5) were observed at pZn 9.5. Analysis of the plant tissues showed that these differences in critical Zn^{2+} activity could be explained based on internal Zn concentrations. At the critical Zn^{2+} activity, the shoot concentration was around 20 mg kg^{-1} dry weight (DW) for all treatments (Fig. 1). These results indicate that Zn complexes indeed contribute to the uptake. The observed uptake fluxes agreed reasonably well with estimated diffusion fluxes, but the uptake flux was larger than the estimated diffusion flux at low Zn supply. We hypothesized that Zn deficiency triggered the root exudation of Zn-complexing organic ligands (resulting in an enhanced diffusion flux), and ongoing experiments support this hypothesis.

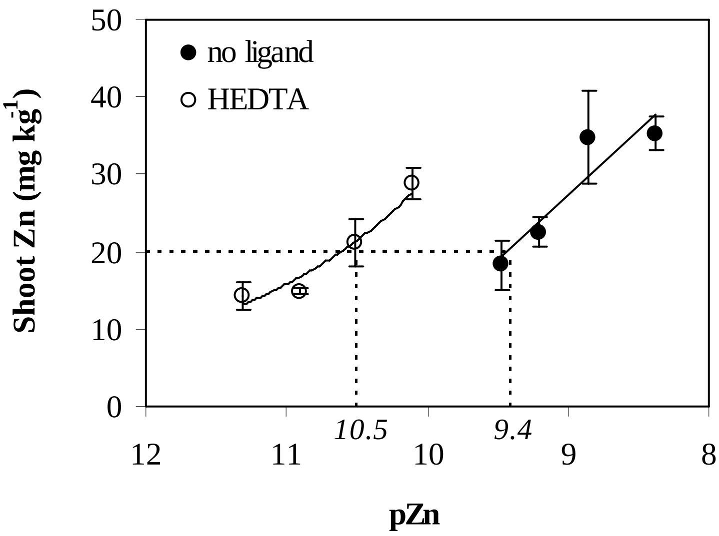

Fig. 1. Zinc concentrations in shoot of tomato grown in HEDTA- or resin-buffered solutions. The dotted lines show the Zn^{2+} activity for which the shoot concentration is 20 mg kg^{-1}.

Zinc uptake by spinach in solutions with different ligands but identical Zn^{2+} activity and total Zn concentration increased as the dissociation of the complex was faster (Table 1), suggesting that the complexes contribute to the uptake by enhancing the diffusion flux.

Table 1. Zinc concentrations and uptake for spinach grown in solutions (with 10^{-9} M Zn^{2+} and 10^{-5} M total Zn) buffered with complexes with varying dissociation rate constants, k_d.

Ligand	logk_d ^A	Root Zn	Shoot Zn	Zn uptake
	(s^{-1})	(mg kg^{-1} DW)	(mg kg^{-1} DW)	(µg per 2 plants)
NTA	>2.0	173	272	70
HEDTA	-3.5	159	124	45
EDTA	-4.2	131	95	39
CDTA	-4.6	84	61	20

CONCLUSIONS

Aqueous complexes increase metal uptake by plants. Therefore, care should be taken in extrapolating results (e.g. critical free ion activities) to other systems, since metal uptake depends on the type and the concentration of the ligand employed.

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